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AN X-RAY STUDY OF *O*-PHTHALIC ACID

By D. M. CHAKRABURTTY

Dept. of General Physics, X-Rays and Magnetism, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 32

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Plates IIA-C

ABSTRACT. From morphological and X-ray study the correct unit cell dimensions for ortho phthalic acid crystal was found to be $a=5.05$A°, $b=14.03$A° $c=9.325$A° and $\beta=93°30'$, number of molecules per unit cell being 4. The extinction conditions of spots from the Weissenberg pictures suggested two space groups C_{2h}^{4} and C_s^1 for the crystal. X-ray analysis, together with chemical consideration and pyro-electric test, suggest the correct space-group for *o*-phthalic acid to be C_s^1 or Cc.

The simple aromatic compound *o*-phthalic acid, a colourless crystalline substance, prepared usually from naphthalene by oxidation, has a molecular formula $C_8H_6O_4$. Morphological and optical studies on this crystal were done earlier, but no attempt has yet been made to determine its complete structure. Becker and Janke (1921) showed that the axial parameters of the single crystals of the substance were $a=9.33$A°, $b=7.13$A°, $c=5.1$A° and $\beta=94°36'$, the number of molecules per unit cell being 2 in that case. Later on, some objections were raised about the crystal class and the value of the angle β by Wyckoff (1931). The present work furnishes, beyond all doubt, the correct unit cell dimensions, the number of molecules in the unit cell and also the space group to which the crystal belongs.

Single crystals of requisite size were obtained from alcoholic solution of the substance. The prominent faces developed were m (210), q (011) and sometimes c (001). Morphological studies made by the present author with the help of a two-circle goniometer, gave the following interfacial angles :

$$m : \bar{m} = 210 : 2\bar{1}0 = 39°4'$$
$$q : \bar{q} = 011 : 0\bar{1}1 = 107°23'$$

Rotation photographs as well as X-ray Weissenberg photographs taken about the three crystallographic axes (Plates IIA, B, C), gave the axial lengths as, $a=5.05$Å, $b=14.03$Å, $c=9.325$Å and the monoclinic angle $\beta=93°30'$. Comparing the values of the unit cell parameters with those found by Becker and Janke (1921) it is seen in the present case that (1) the value of b is doubled and (2) the values of a and c are interchanged. It is obvious that Becker and Janke's values for the parameters are inconsistent with the morophological data. The angle β in the present case is practically the same as Groth's (1917) value obtained by optical methods and is also appreciably different from Becker and Janke's value. The density of the substance was determined by the floatation method and it came out as $1.594 \pm .001$ gm/cm^3 whence the number of molecules per unit cell was found to be 4.

Over-exposed zero layer normal beam Weissenberg pictures about all three axes and equi-inclination pictures for the first and second layer of *a* and *b* were taken in the usual way. The spots were indexed by drawing requisite charts as suggested originally by Schneider (1928). The indices of the spots and their relative intensities are given in Tables I, II and III.

TABLE I

Indexing of spots and their estimated intensities (*c* axis zero-layer)

Plane	Intensity	Plane	Intensity	Plane	Intensity
				510	vvw
200	vs	2(10)0	w	530	w
400	m	2(12)0	w	550	
640	vs	2(14)0	w		ms
660	ms	310	s	570	
080	m	330	m		m
0(10)0	w	350	m		
0(12)0	m				
0(14)0	ms	370	s		
0(16)0	ms	390	m		
110	vs	420	m		
150	ms	440	s		
170	vs	4(10)0	m		
190	ms	4(12)0	m		
220	vs				
260	ms				
280	m				

TABLE II

Indexing of spots and their estimated intensities (*a*-axis zero-layer)

Plane	Intensity	Plane	Intensity	Plane	Intensity	Plane	Intensity
002	s	025	m	04(10)	w	0(10)1	m
004	vs	026	ms	061	s	0(10)2	w
006	m			062	vs	0(10)2	ms
008	vw	027	m	063	s	0(10)4	m
06(10)	m	028	w	064	vs	0(10)5	w
020	vw	029	vw			0(10)7	w
040	vs	02(10)	w	065	w	0(12)1	s
				066	vw	1(12)2	vw
060	ms	041	s	067	vw	0(12)3	m
080	m	042	w	068	w	0(12)4	vw
0(10)0	w					0(12)5	w
0(12)0	m	043	vs	069	m	0(12)6	w
0(14)0	ms	044	m			0(14)1	m
0(16)0	ms	045	w	06(10)	ms	0(14)2	m
021	s	046	m	081	w	0(14)3	w
				082	m	0(14)6	ms
022	vs	047	ms	083	w		
023	vs	048	w	084	m		
024	ms	049	vw	085	m		

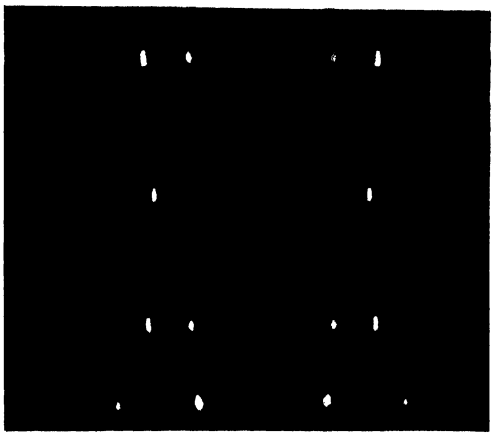

Fig. 1
Rotation picture with c-axis vertical ($r=5{\cdot}0$ cm

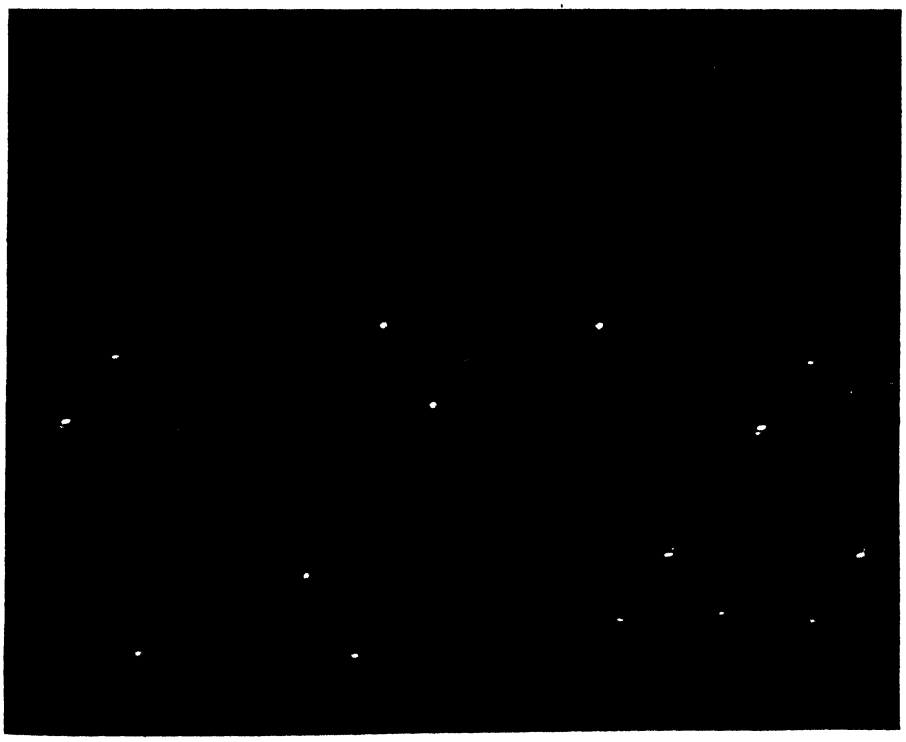

Fig. 2
Normal-beam Weissenberg picture for zero-layer of c-axis

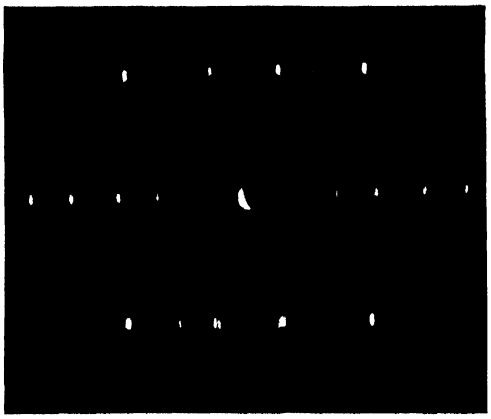

Fig. 3
Rotation picture with *a*-axis vertical ($r = 5{\cdot}0$ cm)

Fig. 4
Normal-beam Weissenberg picture for the zero-layer of *a*-axis

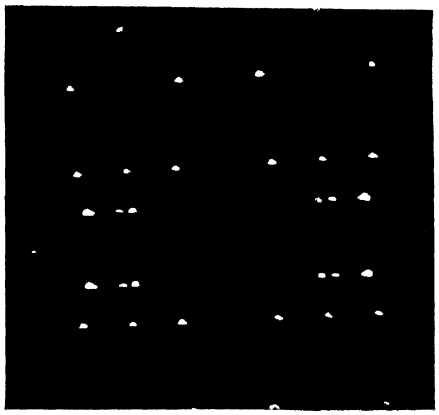

Fig. 5
Rotation picture with *b*-axis vertical ($r = 4{\cdot}5$ cm)

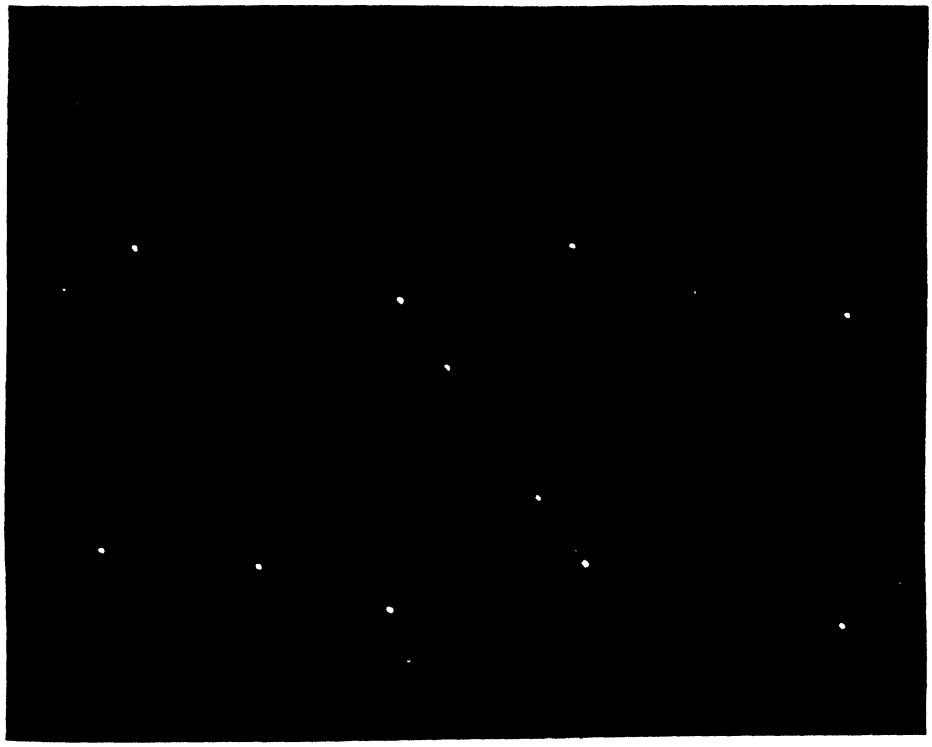

Fig. 6
Normal-beam Weissenberg picture for the zero-layer of *b*-axis

TABLE III

Indexing of spots and their estimated intensities (*b*-axis zero-layer)

Plane	Intensity	Plane	Intensity
200	vs	204	vs
400	m	200	s
002	s	208	m
004	vs	20(10)	s
006	m	402	w
008	w	304	m
00(10)	m	406	w
202	vs		

From the Weissenberg pictures the following conditions for reflections were observed :

(1) *hkl* planes present when $h + k = 2n$

(2) *hol* planes present when $l = 2n$, $h = 2n$

(3) *oko* planes present when $k = 2n$.

These conditions suggest a *c* face-centered lattice for the crystal with a glide plane *c*. These conditions suggest two space groups namely C_{2h}^{6} and C_{s}^{4} for this crystal. The former space groups requires a centre of symmetry while in the latter there is no centre of symmetry. From chemical consideration it is apparent that due to the ortho positions of the two COOH groups in the benzene ring there can be no centre of symmetry for the molecule.

However, definite absence of a centre of symmetry for the crystal was proved by pyro-electric tests, with an improved type of apparatus developed in our laboratory by Basak (1950), based on Lonsdale's (1928 and 1934) work. A crystal of *o*-phthalic acid, approximately 4 mm, was placed between plates of a miniature condenser insulated with mica sheet connected with two insulated copper leads and inserted into a copper tube with one end closed. The wires were taken out through ebonite plug at the mouth of the copper tube, one of the wires being connected to earth and the other to a sensitive tilted gold-leaf electroscope. The plate of the electroscope was given a potential of 1000 volts and the gold leaf was adjusted for the position of maximum sensitivity. The copper tube was immersed suddenly into liquid air. The temperature of the crystal being thus lowered quickly and due to the strain thus set up in the crystal, a small difference of potential was developed on the opposite faces of the crystal which was clearly

indicated by the movement of the gold leaf through about of 3 divisions in the eyepiece scale of the observing telescope. When the copper tube was taken out from the liquid air a similar deflection was observed in opposite direction. This proves beyond doubt the non-existence of a centre of symmetry for the crystal. So we can discard the space group C_{2h}^6 and take C_s^4 or Cc to be the correct space group for the crystal.

A complete structure analysis of the *o*-phthalic crystal by Fourier analysis is under progress.

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